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NUMBER 9

A LABORATORY SPRAY DRIER¹

By A. H. WOODCOCK² AND H. TESSIER³

Abstract

A laboratory model of a cyclone type of spray drier is described. The main drying chamber is an inverted cone 2 ft. in diameter at the base and 5 ft. 2 in. in height. Adjustments are provided for inlet air temperature, total air flow, angular velocity of air in the drying chamber, quantity of liquid introduced, and spraying technique.

The drier has been found practical in operation and has produced dried egg and dried milk equivalent to the best produced commercially.

Introduction

Recent interest in drying as a method of food preservation has increased the commercial use of spray drying equipment. Improvement of both equipment and operation with respect to drying efficiency and product quality have been somewhat hampered by lack of information about some of the factors involved (1, 2). This paper describes a laboratory spray drier designed to study these factors and to produce small quantities of dried material such as may be required for laboratory investigations.

Description of Apparatus

Drier Construction

A cyclone type of drier was selected for the experimental model since this type appeared to be the most suitable. The drier was constructed of 16 gauge galvanized sheet metal with soldered joints and seams, and was insulated with one inch of asbestos cement and one inch of hair felt.

The main drying chamber is shown diagrammatically in Fig. 1. It consists of a cylinder 2 ft. in diameter and 1 ft. 2 in. high from which is suspended the collecting cone, 4 ft. in height. Air enters the chamber from a circular duct around the top through four adjustable louvres that control the rate at which the air revolves in the drying chamber. The exhaust air is removed through a central duct at the top of the drying chamber and the dried material is collected at the bottom of the cone. Two glass windows are provided at the top of the chamber for inspection. No sweep is used to brush dried material

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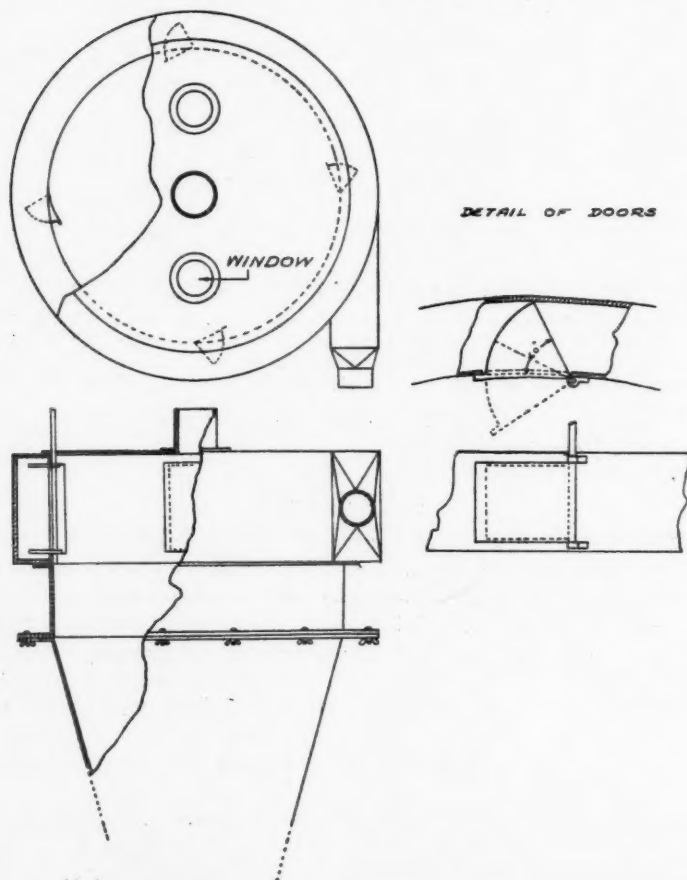


FIG. 1. Diagram of main drying chamber.

off the side of the cone as most of it falls readily off the steep sides. Also, examination of the sides is desirable at the end of a drying period.

The air for the drying operation is supplied to the fan by a fan, similar to the type used on a large household vacuum cleaner, with a maximum capacity of approximately 90 cu. ft. per min. The amount of air used in drying is controlled by orifices placed over the inlet of the fan. Filters may also be connected for bacteriological studies. From the fan the air passes through an electrical heating chamber, supplying 5000 watts, which is thermostatically controlled to maintain inlet air temperatures within $\pm 1^\circ \text{F}$.

Inlet and outlet air temperatures and those at three points down the side of the cone are measured with mercury thermometers.

Static pressures of inlet and outlet air are measured by water manometers connected to small side ducts.

Dust in the exhaust air from the drying chamber is trapped in a small cyclonic type of collector. The angular velocity of the air in the collector may be varied by adjusting the aperture of the inlet port by a slide.

Spray System

The spray nozzle is mounted centrally and projects downwards from the top of the drying chamber. The direct distance from the spray nozzle to the side of the drying chamber is slightly less than one foot, necessitating a very fine spray to obtain a dry product. This condition is obtained by the use of an air atomizer employing compressed air at pressures from 5 to 25 lb. per sq. in.

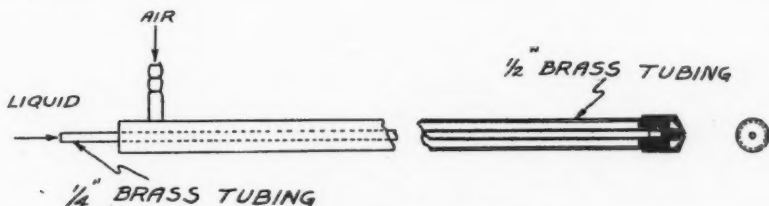


FIG. 2. Diagram of spray nozzle.

A schematic diagram of the spray nozzle is shown in Fig. 2. The liquid to be dried is pumped at a fixed rate through the central tube while compressed air enters through the outer tube protecting the liquid from the heat of the drying chamber until it leaves the nozzle in droplet form. Interchangeable orifices are used for both the liquid and the air and each may be varied independently. Variation in the axial distance between the two orifices is obtained by means of a lock nut on the outer one.

Discussion

The advantages of a small experimental unit are twofold. As a laboratory tool it may be used to dry small amounts of experimental material. As a pilot plant it will give general trends of the effect of various factors on drying efficiency and quality of product.

Difference in size prevents the exact application of the results of laboratory measurements to commercial practice. For example, the proportion of powder that passes over to the dust collector in the experimental unit is greater than in commercial practice. However, factors that reduce the fraction in the dust collector of the experimental unit can reasonably be expected to reduce it in larger plants. The amount of insulation on the laboratory unit is also a function of size. The amount used on this unit was not excessive although the drop in temperature due to conduction through the walls is higher than

for commercial units. This temperature drop is to be expected since the ratio of surface area to volume is greater in the laboratory model.

The maximum capacity of the drier is of the order of four litres of liquid per hour. It has been used to obtain samples of dried milk, egg, and Irish moss of excellent quality.

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SEDIMENTATION VOLUMES AND ANOMALOUS FLOW IN LYOPHOBIC SUSPENSIONS¹

BY WILFRED GALLAY² AND IRA E. PUDDINGTON²

Abstract

The sedimentation volumes of starch, magnesium oxide, ferric oxide, and talc in a series of liquids have been measured. The results are greatly influenced by the presence of small quantities of water. Increase in sedimentation volume is related to the degree of flocculation in the system, leading to a branched-chain scaffolding type of structure. Viscosity determinations show that such structures possess rigidity, which is absent in systems showing a small sedimentation volume. The effect of flocculation is particularly large in suspensions of anisodimensional particles.

The volume occupied by a finely divided solid in a liquid, inert with regard to the suspensoid, and the texture and flow properties of the suspension are of considerable importance in a number of chemical industries. It is well known that the equilibrium sedimentation volume of a given weight of a solid of definite particle size varies with the type of liquid in which it is suspended, and two general hypotheses have been set up in attempts to explain these differences.

Ostwald and Haller (10) have advanced the concept of lyosorption, involving a lyosphere of varying thickness of adsorbed and compressed liquid on the surface of the particle, to explain the differences obtained with a given suspensoid in a series of liquids. They obtained essentially the same order with various solids in a series of liquids, ranging from larger volumes in non-polar liquids to smaller volumes in polar liquids, and noted that there was some correlation between the dielectric polarization value of the liquid and the sedimentation volume in that liquid. Lyosorption has been accepted as an explanation also by other workers (5, 7, 13).

It has been shown also that a large sedimentation volume is accompanied by a degree of flocculation of the suspensoid (3, 8, 11, 12), and von Buzagh (1) has noted quantitatively that the force of adhesion between the particles varies with the suspension medium used. Flocculation must be accompanied necessarily by an increased sedimentation volume, as shown diagrammatically in Fig. 1. If the particles are independent of one another during settling, they can slide past one another to form a compact sediment of low volume. If,

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on the other hand, the particles stick to one another, a scaffolding type of structure must result which leads to a considerably increased volume. Such an explanation for the variation in sedimentation volume in various liquids has also been advocated (3, 6). The relation of the wetting power of the liquid for the solid in this connection has also been discussed (2, 9, 11).

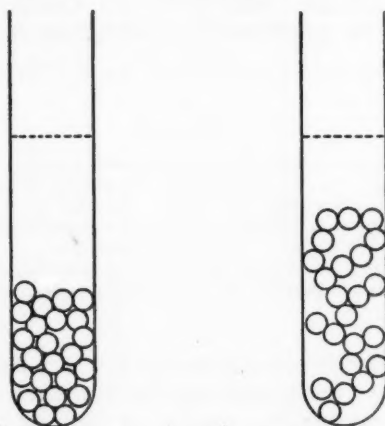


FIG. 1. Diagrammatic representation of increased sedimentation volume due to flocculation.

It is to be noted particularly that previous investigators in this field have laid stress especially on the possible effect of the polarity of the liquids used, and scant attention has been paid to the presence or absence of small quantities of water in the systems under investigation.

In the present work, experiments were carried out using carefully dried solids in specially dried organic liquids, and the possible effect of moisture was thus determined.

TABLE I
SEDIMENTATION VOLUMES OF STARCH

Suspension	Sedimentation volumes, cc.	
	Corn starch	Potato starch
Air-dry starch in water	9.9	8.4
Air-dry starch in dry xylene	10.3	11.1
Vacuum-dried starch in dry xylene	7.8	6.5

Table I shows the effect of the moisture contained in starch on sedimentation volumes in water and in dry xylene. The volumes are corrected for starch on a dry basis.

The effect of water in increasing the settling volume of starch in xylene is very great. The following observations were noted also in a comparison of the air-dry and vacuum-dried starch in dry xylene:

- (1) The velocity of sedimentation is greatly accelerated when water is present.
- (2) When settling has approached equilibrium, the supernatant liquid is clear in the presence of water, and is cloudy in the absence of water.
- (3) More light is transmitted by the settled suspension in the presence of water.
- (4) Flocculation of the starch granules is clearly observed in the presence of water.
- (5) The settled starch forms a highly compact sediment in the absence of water, and a much more readily dispersible sediment in the presence of water.

These observations all point directly toward a flocculation of the starch in the presence of moisture. The flocculates settle more rapidly and there are no individual granules, which would leave a cloudiness in the liquid. The branched-chain scaffolding structure allows more light through, occupies a much greater volume after settling, and the structure is readily disrupted by shaking. The particles adhere to one another strongly in the presence of a small quantity of water, and are independent of one another in the absence of water.

It is noted further that although starch occupies a greater volume in xylene than in water, the sedimentation volume in dry suspension in xylene is considerably less than in water. The degree of independence of the starch granules in a dry organic solvent is therefore much greater than in water. The extent of flocculation is thus not directly related to the wetting of the solid by the liquid, since the effect of a small quantity of water is quite different from that of a large quantity of the same liquid.

This effect of moisture and also that of the polarity of the liquid were investigated in a further series of sedimentation experiments, and the results are shown in Table II. All the suspensions consisted of 5 gm. of potato starch in 80 cc. of liquid, and the results are expressed as height of sedimented column (cm.) in tubes of standard diameter. The liquids were all carefully dried. The air-dry starch contained about 17% moisture.

The same observations were noted in this series with regard to the flocculation and attendant effects obtained in the presence of water. It is noted that the sedimentation is much greater in the presence of water in the non-polar liquids, whereas the difference is small in the polar liquids. Using air-dry starch, a large difference between polar and non-polar liquids was obtained, in corroboration of the results reported by the previous workers noted above. In the anhydrous suspensions, however, there is no appreciable difference in the sedimentation volumes in this series. The effect in starch suspensions is shown therefore to be due to the presence of moisture in the suspensions, and

TABLE II
SEDIMENTATION OF STARCH IN VARIOUS SUSPENSIONS

Suspension medium	Vacuum-dried starch		Air-dry starch	
	24 hr.	2 months	24 hr.	2 months
	Sedimentation value, cm.			
Xylene	1.92	1.88	3.11	2.99
Benzene	1.91	1.95	2.99	2.95
Chloroform	1.97	1.98	*	*
Ethyl alcohol	1.89	2.05	2.41	2.28
Acetone	1.90	2.05	2.39	2.26

* The suspension showed creaming.

cannot be due to any physical property of the liquid, such as dielectric constant or dielectric polarization.

The effect of varying quantities of water on the sedimentation volume of starch in such suspensions was then investigated. Five grams of vacuum-dried potato starch was suspended in 90 cc. of dry suspension medium and the sedimentation volume was read after 48 hr. Then successive quantities of 0.25 cc. of water were added, and the settling volume was measured in each case after 48 hr. The final volume after the total addition of 1.25 cc. of water was measured again after 14 days. Table III shows the results obtained.

TABLE III
EFFECT OF WATER ON THE SEDIMENTATION VOLUME OF STARCH

Suspension medium	Water added, cc.						
	0.0	0.25	0.5	0.75	1.0	1.25	1.25 (14 days)
	Sedimentation volume, cc.						
Petrol ether	6.9	8.0	9.1	10.4	12.0	16.5	16.1
Benzene	6.4	7.5	10.0	11.7	13.5	17.1	17.0
Chloroform	6.5	7.0	11.0	—	30.0	33.0	31.2
Ethyl ether	6.2	6.2	7.0	7.5	7.8	8.3	8.6
Ethyl alcohol	6.5	7.2	8.5	8.4	8.4	8.5	8.5
Water*	6.5	—	—	—	—	—	—

* Air-dry starch used. Vacuum-dried starch yields a larger volume (9.2 cc.) in water, owing to a special hydration effect discussed elsewhere (4).

In this series also it is noted that the type of liquid has no appreciable effect on the sedimentation volume of starch in dry suspensions. The addition of water increases the volume in non-polar liquids but has only a small effect in polar liquids.

Similar experiments were carried out with dry magnesium oxide and the results are shown in Table IV.

TABLE IV
SEDIMENTATION VOLUMES IN MAGNESIUM OXIDE SUSPENSIONS

Suspension medium	Water added, cc.						
	0.0	0.25	0.5	0.75	1.0	1.25	1.25 (14 days)
	Sedimentation volume, cc.						
Petrolie ether	11.0	11.5	12.0	12.0	13.7	14.0	14.0
Benzene	12.2	12.0	13.0	14.7	13.0	14.6	14.0
Chloroform	11.1	11.2	14.0	14.0	13.0	13.0	12.1
Ethyl ether	11.2	10.4	11.0	11.3	10.4	10.6	9.8
Ethyl alcohol	10.5	10.0	10.2	10.4	10.2	10.2	9.5
Water	10.5	—	—	—	—	—	—

In suspensions of magnesium oxide also, the settling volume is relatively little affected by the type of liquid in water-free suspensions. With the addition of water, flocculation is brought about in the non-polar liquids and the settling volume is therefore increased.

Table V shows results obtained in similar sedimentation tests with ferric oxide.

TABLE V
SEDIMENTATION VOLUMES IN FERRIC OXIDE SUSPENSIONS

Suspension medium	Water added, cc.						
	0.0	0.25	0.5	0.75	1.0	1.25	1.25 (14 days)
	Sedimentation volume, cc.						
Petrolie ether	5.5	10.5	12.5	12.2	8.2	6.0	5.8
Benzene	6.5	11.0	15.0	14.6	11.5	7.5	7.5
Chloroform	6.2	9.8	14.8	14.7	12.0	10.0	11.0
Ethyl ether	5.2	6.8	7.0	8.0	9.0	10.8	11.0
Ethyl alcohol	5.3	5.2	5.3	5.5	5.5	5.5	5.0
Water	5.3	—	—	—	—	—	—

The flocculating effect of water is again evident in this series and it decreases with increasing polarity of suspension medium. In this case it is noted that the sedimentation volume in the non-polar media decreases strongly with large quantities of water. The values approach those obtained in pure water.

Table VI shows results of similar experiments with talc.

It is noted that the effect of added water is particularly large in this series. In this connection it is interesting to note that the solid particles are highly anisodimensional in shape, and flocculation therefore tends toward a par-

TABLE VI
SEDIMENTATION VOLUMES IN TALC SUSPENSIONS

Suspension medium	Water added, cc.						
	0.0	0.25	0.5	0.75	1.0	1.25	1.25 (14 days)
	Sedimentation volume, cc.						
Petrolie ether	12.0	25.0	35.0	34.0	28.0	27.2	27.0
Benzene	12.0	30.1	36.0	37.1	31.0	29.1	28.3
Chloroform	12.2	33.2	44.0	42.0	36.0	35.0	34.5
Ethyl ether	10.5	14.0	17.8	23.0	21.0	22.5	22.0
Ethyl alcohol	9.0	8.6	8.8	8.5	8.4	9.0	8.4
Water	9.8	—	—	—	—	—	—

ticularly large sedimentation volume. The decrease in volume with larger quantities of water is again observed with the non-polar media.

Fig. 3 shows photographs of settled suspensions of talc and of starch, in which the effect of a small quantity of water on the sedimentation volume is strikingly apparent.

Flocculation of a suspenoid leading to a scaffolding structure in the suspension should result in an alteration in flow characteristics. Such a structure possesses an appreciable degree of mechanical strength and hence a minimum force must be applied in order to disrupt the structure and bring about flow. The system will show a well defined yield value. The viscosimeter used was a Goodeve Thixoviscometer, well adapted to show the effect of shearing stress on the degree of flow. The viscosities of the following suspensions were determined: (1) 20% of dry talc in dry benzene, (2) 20% of talc in benzene containing 0.5% of water, (3) 40% of dry potato starch in dry xylene, (4) 40% of potato starch in xylene together with 10% of water.

Fig. 2 shows the results obtained. The calibration curve of the oil shows a straight line relation between flow and pressure. The influence of a small quantity of water on a talc suspension is shown not only in the large decrease in the mobility of the suspension but also in the establishment of a large yield value. In the starch suspensions, a small yield value is brought about by the addition of the water. In these suspensions containing water, flow was brought about by a minimum shearing force, following which the flow-pressure relation is linear as in the case of unflocculated suspensions. The mobility is decreased owing to the residue of agglomerated particles and the continuing tendency for the original structure to re-form.

The flocculation discussed is readily observed macroscopically. Fig. 4 shows photographs of a suspension of 5% of dry talc in alcohol containing 1.25% of water, in comparison with a suspension in benzene containing 1.25% of water. The photographs were taken during initial settling. The large flocculates brought about by the water in the non-polar medium are clearly

seen and it is noted also that the supernatant liquid is clear in that suspension. It was previously shown that the addition of water has little effect on suspensions in alcohol. Figs. 5 and 6 show photomicrographs of air-dry and dried starch respectively in dry benzene, taken between crossed Nicols. The agglomerating effect of the water contained in the air-dry starch is very apparent.

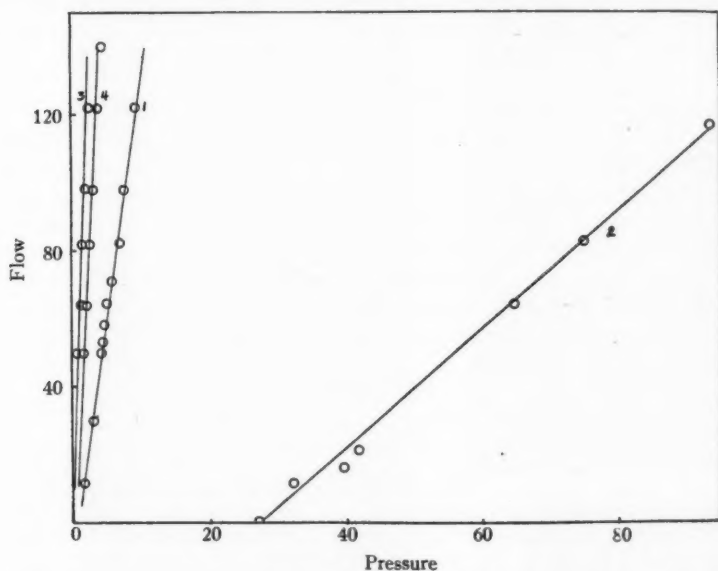


FIG. 2. Flow-pressure curves in suspensions: 1, 20% of dry talc in dry benzene; 2, 20% of talc in benzene containing 0.5% of water; 3, 40% of dry potato starch in dry xylene; 4, 40% of potato starch in xylene with 10% of water.

The concept of lyosorption, or the existence of lyospheres of strongly bound liquid around each particle, as a direct explanation of the differences in settling volume obtained in various suspensions, would appear to be untenable in the light of the results described above. It would appear rather that the difference in settling volumes is a function of the degree of flocculation of the suspended particles. The resulting increase in volume is relatively large for essentially anisodimensional particles such as talc, and is small for particles of starch that approach the spherical. The shape of the particle will influence also the difference in viscosity due to flocculation, as a result of the strength of intermeshing of the particles in the scaffolding structure. Adsorption of liquid on the particles must involve a gradation in the force with which the liquid is held, and such a system would not be expected to show a yield value but rather a curve for the flow-pressure relation convex to the pressure axis.

The dependence of the degree of flocculation on the wetting power of the liquid or liquids used would appear to involve some complicated factors. In the presence of water only, or when polar liquids are totally excluded, the

suspended particles show virtually complete independence, with the accompanying factors of close packing and low sedimentation volume. The scaffolding structure brought about by the presence of a small or moderate amount of water together with a non-polar medium must be the result of a force of attraction between adjacent surfaces at least partially wet with water. It is quite probable that the sticking is due to hydrogen bonds between water layers, in a system in which there is insufficient water available to act as a medium of complete wetting.

Experimental

Magnesium oxide, talc, and ferric oxide were dried by heating to 1000° C. overnight. Starch was dried by heating to 45° C. *in vacuo*. Petrolic ether was distilled from phosphorus pentoxide. Benzene was distilled and the first and last fractions discarded. Chloroform was dried over potassium carbonate and distilled, the first and last fractions being discarded. Ethyl ether was dried over sodium hydroxide, distilled, redried with calcium chloride, redistilled and finally distilled from phosphorus pentoxide. Absolute alcohol was distilled from potassium hydroxide.

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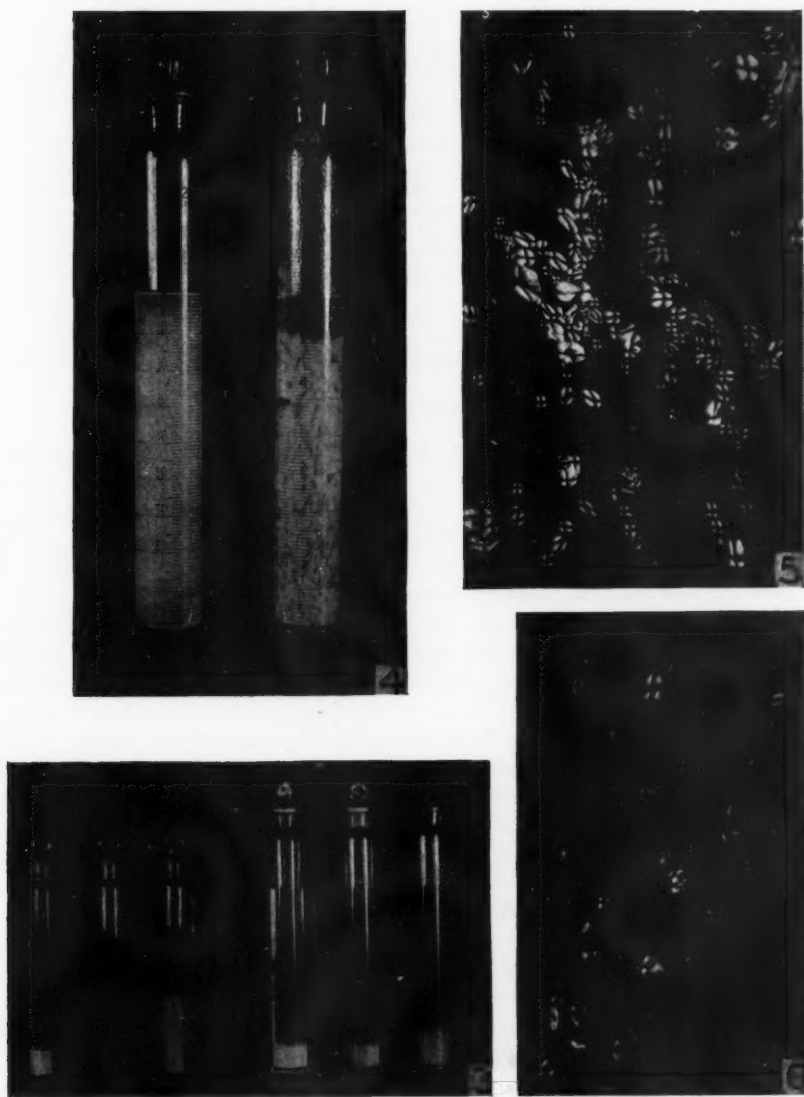


FIG. 3. Settled suspensions of talc (smaller graduates) and starch (larger graduates). Suspension medium, from left to right in each group, is water, dry benzene, and benzene containing a small quantity of water.

FIG. 4. Sedimentation of dry talc in, left, ethyl alcohol containing 1.25% of water, and right, benzene containing 1.25% of water.

FIG. 5. Photomicrograph (crossed Nicols) of air-dry starch in dry benzene.

FIG. 6. Photomicrograph (crossed Nicols) of dried starch in dry benzene.



THE HYDRATION OF STARCH BELOW THE GELATINIZATION TEMPERATURE¹

BY WILFRED GALLAY² AND IRA E. PUDDINGTON²

Abstract

The dilatancy of an aqueous starch suspension is particularly marked just above the freezing point and decreases with rise in temperature. The sedimentation volume increases correspondingly, and the degree of compactness of the sediment decreases with increase in temperature. Flocculation is apparent at temperatures 10° below the gelatinization point. It is concluded that there is a continuous increase in hydration of the starch with temperature, in the range below the gelatinization point. The hydration below the gelatinization point is essentially reversible.

Dried starch shows little or no dilatancy and a lowering in gelatinization point, and it is noted that the relatively large heat of wetting is probably responsible, in that a degree of gelatinization is effected at the surface of the granule.

Anomalous Flow in Starch Dispersions

Aqueous starch suspensions at ordinary concentrations, e.g., up to about 40% by volume, exhibit Newtonian flow, with no yield point or deviation from linearity in the flow-pressure relation.

If the starch is subjected to any degree of gelatinization, then deviations from this normal type of flow may be detected even at very low concentrations in the suspensions, and the extent of these deviations increases sharply with concentration. With increasing pressure, the flow increases more rapidly, so that the flow-pressure curve is convex to the pressure axis. There is no yield point and it is probable that the decrease in viscosity at higher driving pressures is brought about by a deformation and orientation of the dispersed particles in the direction of a lessened internal friction. Such flow behaviour has been termed structural viscosity and is commonly exhibited by most lyophilic colloidal dispersions containing anisodimensional particles.

Under some conditions, a flocculation of the starch particles in a suspension may result in the establishment of a structure. This is readily observed in a suspension of moist starch (2) in a non-polar medium. A yield point, indicating the force necessary to disrupt the structure, is then observed, and this is followed by linearity in the flow-pressure relation. Such flow behaviour is commonly termed thixotropy and is characterized by a considerable decrease in viscosity on the application of a disturbing force, e.g., stirring or shaking.

In aqueous suspensions of ungelatinized starch at high concentrations, e.g., above about 40% by volume, the flow is again anomalous, and such suspensions show dilatancy to a marked degree. Dilatancy (1) is essentially opposite

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² Chemist.

in character to thixotropy or structural viscosity, in that the resistance to deformation increases with the stress. If a quantity of such a suspension is taken up in the palm of the hand, increased firmness is noticed as pressure is exerted by closing the fingers. If the hand is then opened, the mass becomes liquid in character and flows. When a beaker containing such a concentrated starch suspension is tilted, the suspension flows. The same suspension can be cut with a spatula as though it were solid, but following the withdrawal of the applied force, the portions of the suspension flow readily. On stirring, the resistance offered by the suspension increases with the stirring force. For the same reason, a weight dropped on to the suspension contained in a vessel will have its speed reduced to much the same extent regardless of the height of fall of the weight.

Dilatancy is a property shown only by suspensions of essentially isodimensional particles, in which the particles are independent of one another. This independence is manifested in several ways, viz.:

- (1) The suspensions possess a small sedimentation volume.
- (2) Settling is relatively slow, and this sediment is closely packed.
- (3) Increasing stresses, such as stirring, meet with increasing resistance, owing probably to a close packing of the particles ahead of the applied force.

Any degree of interdependence of the particles leading to flocculation results in a corresponding decrease or eventual complete absence of dilatancy. The extent to which a starch shows dilatancy, therefore, either as such or as manifested by the relative magnitude of the sedimentation volume, may be taken to be a measure of the hydration of the starch. The ability of the starch granules to slide past one another during settling to form a compact sediment with low sedimentation volume is a measure of the independence of the granules, and even a very small amount of sticking, with consequent small increase in sedimentation volume, is sufficient to destroy to a large extent the property of dilatancy.

The factor of concentration is important not only for the appearance of the phenomenon itself, but as a further indication of the probable underlying mechanism. Dilatancy is obtained only within a relatively narrow range of concentration. In more dilute suspensions, it is apparent that close packing is difficult to attain by applied forces, and in suspensions of too high a concentration, the system is a solid at rest. Within a narrow range, an applied force can bring about a movement of the granules so as to cause a temporary close packing in the region affected by the force. The system is entirely reversible and the original texture is observed when the system is at rest.

Microscopic observations lend direct evidence for this explanation. If such a dilatant suspension is observed under the microscope and a force is applied by means of a fine glass rod, the starch granules are seen to flow past one another in the region ahead of the force, and a condition approximating a close packing is observed. When the movement of the rod is stopped, the

granules flow again so that the previously affected region presents again the same picture of concentration as other regions on the slide. In non-dilatant systems, on the other hand, such as in suspensions of moist starch in non-polar media, the particles are seen to be partially flocculated, and stirring serves only to effect some break-up of these flocculates. It is to be noted therefore that (i) the factor of independence among particles is necessary in order to enable the granules to slide past one another, and (ii) the factor of concentration is important so that a relatively small increase in concentration brings about a condition approximating close packing, and a solid condition is reached.

Dilatancy may be measured quantitatively by means of a flow-pressure curve or qualitatively by stirring by hand with a spatula; a qualitative measurement of this kind is quite sensitive to small changes in dilatancy. Fig. 1 shows flow-pressure relations in several aqueous starch suspensions measured in a modified Stormer type of viscosimeter.

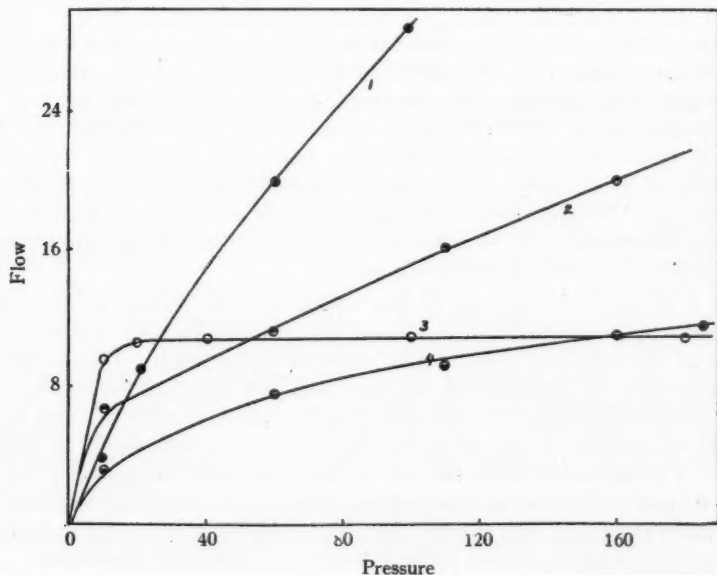


FIG. 1. Flow-pressure relations in aqueous starch suspensions. 1, 2, and 4, partially dilatant; 3, highly dilatant.

Effect of Temperature

At temperatures above the gelatinization point, the granules swell visibly and the suspensions show a rigidity in the flow-pressure curve. It is of importance, however, to determine whether changes occur also below the gelatinization temperature, and a series of experiments were carried out to determine the effect of temperature on sedimentation volume and dilatancy.

The potato starch and distilled water were brought separately to the desired temperature, then thoroughly mixed, and the suspensions were allowed to settle at the corresponding temperature. After equilibrium had been attained, the ease of redispersion of the sediment was measured by a determination of the number of shakings necessary for dispersion. Table I shows the results obtained for suspensions containing 50 gm. of potato starch.

TABLE I

Temp., °C.	Sedimentation volume, cc. after 16 hr.	Number of shakings to redisperse
3	66.5	250
25	69.0	110
38	70.1	120
50	71.2	84

It is noted that the sedimentation volume increases with temperature. There was visible evidence also of some flocculation at the highest temperature. It is noted also that the compactness of the sediment is very great at the lower temperatures. At 50° C., however, as a result of flocculation, the sediment is much more readily dispersed. There was relatively very little dilatancy at 50° C., and this property increased greatly with decrease in temperature. No appreciable increase in volume of the granules was detectable microscopically at 50° C., and this points further to a scaffolding structure in the suspension resulting from flocculation.

Fig. 2 shows a comparison of the actual specific volume of the starch (measured by pycnometer in a mineral oil medium) and the sedimentation volume of the starch in water, over a range of temperature. It is noted that the coefficients of expansion in the two cases are widely different, and this result indicates further that the differences in sedimentation are due to differences in packing or due to an increase in volume as a result of swelling action. Furthermore, when the starch that had been suspended at 50° C. was dried and redispersed at room temperature, it was found that a sedimentation volume of 68.7 cc. was obtained (original value 69.0 cc.), and the dilatancy was correspondingly greater. The hydration is therefore reversible.

Effect of Drying

The observation was made that when starch was extensively dried, e.g., at 45° C. *in vacuo*, the resultant dried starch when dispersed in water at room temperature showed no dilatancy. It appeared therefore that drying of starch had an important effect on its hydration capacity. The sedimentation of dried starch in organic liquids has been discussed elsewhere (2).

Samples of potato starch were dried by various means, and the sedimentation volume of the dried starches was determined. The

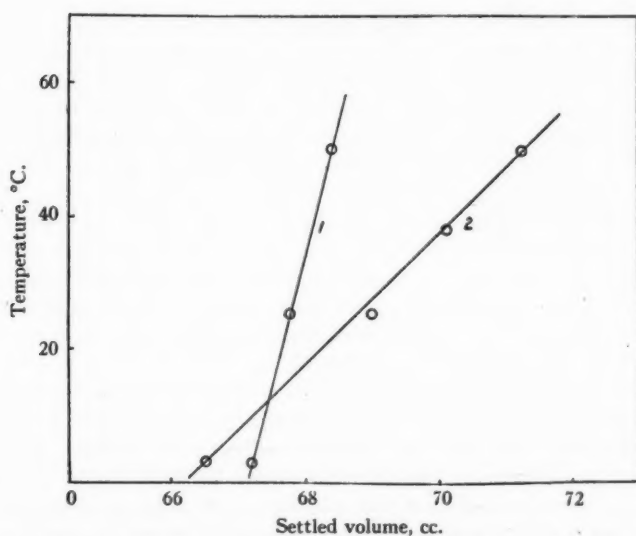


FIG. 2. Specific volume and sedimentation volume of starch in aqueous suspension over a range of temperature. 1, specific volume; 2, sedimentation volume.

moisture absorption was determined also after exposure to 100% relative humidity for a week. The gelatinization point of the starches before and after moisture regain was determined as follows. A 10% suspension of the starch in distilled water, contained in a test-tube, was slowly heated in a water-bath, a constant temperature gradient being maintained between starch suspension and heating bath. The suspension was slowly stirred with a thermometer, and the temperature at which there was a sudden change in the viscosity and in the appearance of the suspension was noted. By maintaining all factors as constant as possible, this standard method gave results reproducible to $\pm 0.1^\circ\text{C}$. Moisture contents of the dried starches were determined in toluene by the Dean and Stark method. Table II shows the results obtained.

TABLE II

Drying method	Water, %	Water regain (dry starch basis), %	Sediment- ation vol., cc.	Gelatinization point	
				Dried starch	After moisture regain
Air-dry starch	15.5	35.5	8.1	60.5	61.2
Air-dry starch	15.5	35.3	—	—	61.0
Over H_2SO_4 , 2 weeks	3.8	34.1	10.0	58.6	59.6
Heated at 80°C ., 48 hr.	1.0	32.5	9.6	57.7	59.8
Heated at 105°C ., 24 hr.	0.6	30.0	9.7	56.1	59.6
<i>In vacuo</i> at 25°C ., 96 hr.	0.5	32.1	9.8	56.7	59.2
<i>In vacuo</i> at 45°C ., 48 hr.	0	30.9	9.7	55.5	60.5

It is noted that drying causes a considerable increase in the sedimentation volume, in corroboration of the previous observation of decreased dilatancy. The gelatinization point is also lowered by drying. After the dried starches are allowed to regain moisture, the gelatinization values are restored to virtually the original values. The sedimentation volumes and dilatancy also return to the original values for the undried starch, and it would appear therefore that the increased hydration shown by the dried starches results in a slight swelling or gelatinization at a lower temperature. A starch showing a sedimentation volume of 8 cc. was dilatant, a starch with a sedimentation volume of 9 cc. was only partially dilatant, and when the sedimentation volume was 10 cc., dilatancy was absent entirely. By allowing the dried starch to regain moisture, the sedimentation volume was restored to 8 cc. and the starch then showed strong dilatancy.

It was then noted that if a small quantity of dried starch was added to a large quantity of water in a container capable of rapid heat transfer or of high heat capacity, and the suspension concentrated by settling, the resultant suspension then retained a considerable degree of dilatancy. On the other hand, when 25 gm. of dried starch was added to 20 cc. of water in a glass vessel, the temperature of the mixture rose from 25° to 40° C., and the suspension showed no dilatancy. When this suspension was then dried at room temperature, a degree of dilatancy was restored on redispersion.

It appeared therefore that the heat of wetting of the starch in water was of considerable importance. The heat of wetting was simply measured by adding 10 cc. of water to 5 gm. of the starch contained in a Dewar flask of 50 cc. capacity, and then noting the maximum temperature attained after mixing. Table III shows results obtained in measurements of such heat effects.

TABLE III
HEAT OF WETTING OF DRIED STARCHES

Method of drying	Moisture (dried starch), %	Rise in temp., °C.
<i>In vacuo</i> at 45° C., 48 hr.	0	11.5
<i>In vacuo</i> at 25° C., 96 hr.	0.5	9.0
Heated to 105° C., 24 hr.	0.6	9.0
Heated to 80° C., 48 hr.	1.0	8.8
Over H ₂ SO ₄ , 3 weeks	3.8	8.5
Not dried	16.0	2.3

The relatively large amount of heat evolved in systems of such heat capacity would appear to point clearly to a much greater heat rise at the surface of the granules and an accompanying excessive hydration resembling gelatinization. This effect is sufficient to account for the change in physical properties of suspensions, resulting from drying of the starch. Incipient gelatinization at the surface of the granules leads to sticking and agglomeration, thus

increasing the sedimentation volume and destroying dilatancy, which results from the independence of the granules. The gelatinization point is lowered also since subsequent hydration at the higher temperature is more easily effected after the initial surface change has been brought about.

Air-dry starch (45 gm.) was heated to 50° C. for two hours and added quickly with stirring to water (45 cc.) at room temperature. The resultant suspension was only partially dilatant. With a starch preheated to 75° C. in a similar experiment, the dilatancy was largely destroyed, and on drying the starch at room temperature, and redispersing in water at room temperature, the dilatancy was not recovered.

A suspension of air-dry starch in water that showed marked dilatancy was heated in an oven maintained at 50° C. for one and one-half hours, after which time the temperature of the starch suspension had risen to 45° C. Viscosity determinations then carried out at room temperature showed that the dilatancy had been partially destroyed. This would appear to be a further indication of a definite swelling or hydration of the starch at temperatures considerably below the gelatinization temperature.

Starches dried under various conditions were gelatinized in water at 75° C., and the viscosities measured in a torsional viscosimeter. It was found that the starch dried at 105° C. for 24 hr. was considerably altered, in that the paste prepared from it showed a reduced viscosity. There was no appreciable difference in the viscosity of other dried starches.

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THE SYNTHESIS OF 2-KETOCYCLOHEXYLSUCCINIC ACID AND RELATED SUBSTANCES

III. SYNTHESSES INVOLVING ETHYLENE AND PROPYLENE OXIDES¹

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D. S. ALEXANDER⁵

Abstract

2-Oxotetrahydrofuran-3-acetic acid is produced when ethylene oxide, ethyl sodiomalonate, and ethyl chloroacetate are condensed and the resulting ester is hydrolysed and decarboxylated. If ethyl β -bromopropionate is used in place of ethyl chloroacetate, 2-oxotetrahydrofuran-3-propionic acid results.

Condensation of propylene oxide with ethyl malonate in the presence of sodium ethylate, followed by hydrolysis and decarboxylation, yields γ -valerolactone (2-oxo-5-methyltetrahydrofuran) in rather poor yield.

The β -halogenated esters may be replaced in condensations of this nature by benzyl chloride, 2-oxo-3-benzyltetrahydrofuran being produced.

Introduction

The synthesis of the γ -lactone of cyclohexanolsuccinic acid by McRae, Charlesworth, and Alexander (9) from cyclohexene oxide suggested that this method might be extended to other ethylenic oxides. Such condensations between sodio-activated methylene groupings and ethylenic oxides have been rather infrequent. Traube and Lehmann (13, 14) condensed ethylene oxide with ethyl sodiomalonate and on acidification obtained 2-carbethoxybutyrolactone. Similarly, from epichlorohydrin they obtained 4-chloromethyl-2-carbethoxybutyrolactone. They also carried out other condensations in which the malonic ester was replaced by acetoacetic ester. Haller and Blanc (3) used this type of condensation in a synthesis of terebic acid from ethyl β,β -dimethylglycidate. The reaction has been employed by Coffey (2) and by Kendall, Osterberg, and MacKenzie (6) with cyclohexene oxide.

When the sodium salt resulting from the condensation of ethylene oxide and ethyl sodiomalonate was treated with ethyl chloroacetate and the product was hydrolysed, 2-oxo-3-carboxytetrahydrofuran-3-acetic acid (I) was formed. On decarboxylation this gave 2-oxotetrahydrofuran-3-acetic acid (II). On treatment of II with alcoholic ammonia under pressure, the lactone ring opened and the diamide (III) was formed. Reference to the lactonic acid (II), its ester, and the barium salt of the corresponding β -hydroxyethylsuccinic acid are found in the work of Weidel and Hoff (15), who obtained their products from isonicotinic acid and cinchomeronic acid by reduction with sodium

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Contribution from the Departments of Chemistry, University of Manitoba, Winnipeg, Man., and Queen's University, Kingston, Ont.

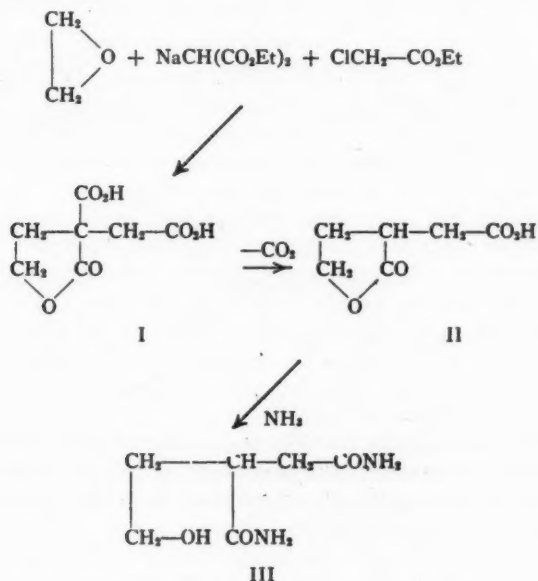
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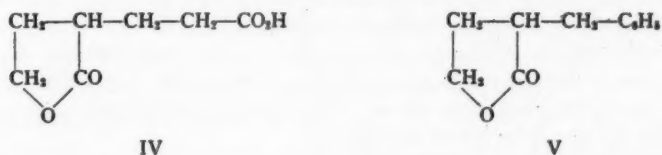
⁵ Holder of a Bursary under the National Research Council of Canada, 1939-1940.

amalgam. The somewhat meagre information in Beilstein* did not permit a comparison to be made.



When ethyl β -bromopropionate was employed in this condensation in place of ethyl chloroacetate, 2-oxotetrahydrofuran-3-propionic acid (IV) resulted as the final product.

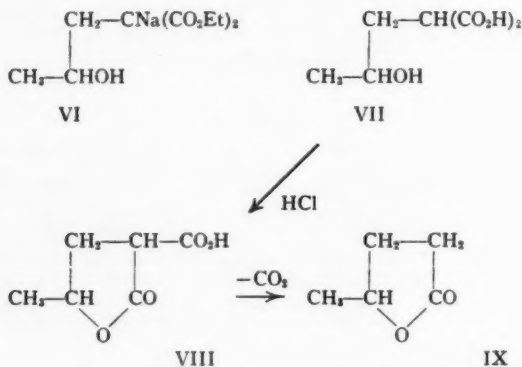
β -Halogenated esters may be replaced in condensations of this nature by benzyl chloride, in which case 2-oxo-3-benzyltetrahydrofuran (V) resulted. It would seem probable that alkyl side chains in the 3-position might be introduced, as has been done by McRae, Charlesworth, and Alexander (9).



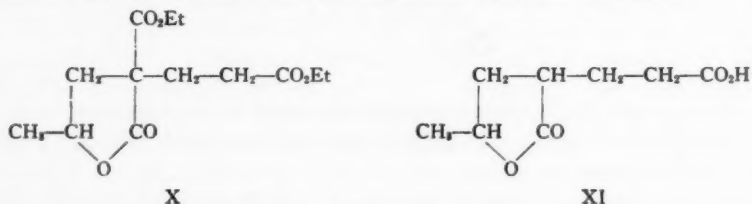
When propylene oxide was condensed with ethyl sodiomalonate, and the diester (VI) saponified, the acid (VII) was isolated in the form of a barium salt. On acidification, 2-oxo-5-methyltetrahydrofuran-3-carboxylic acid (VIII) resulted. This was found to be comparatively unstable, and was decarboxylated to give γ -valerolactone (IX), seemingly identical in properties with that

* Beilstein, *Handbuch der organischen Chemie*, 4th ed. III, 452; XVIII, 374.

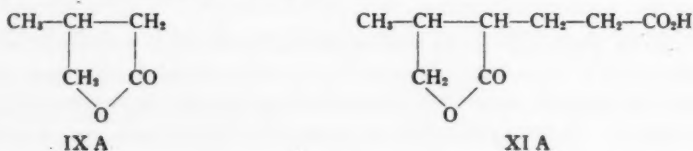
produced by Schuette and Thomas (12) and several other authors (1, 8, 11) by the reduction of laevulinic acid.



When the sodio-derivative (VI) was condensed with ethyl β -bromopropionate, the ester lactone (X) resulted, and, on hydrolysis and decarboxylation 2-oxo-5-methyltetrahydrofuran-3-propionic acid (XI) was obtained.



In all these condensations the formation of a secondary alcohol and the addition of the ethyl malonate addendum to the unsubstituted carbon of the ethylenic oxide system is in agreement with the reaction of propylene oxide and Grignard reagents as reported by Henry (4) and Hess (5). However, it is difficult to obtain pure products and substantial yields from these propylene oxide condensations. This is probably due to the fact that the 4-methylbutyrolactonic substances illustrated are accompanied by smaller amounts of the 3-methylbutyrolactone series. The isomeric substances corresponding to IX and XI would be IX A and XI A.



Hess (5) actually reports the isolation of an isomer, possibly of this nature, in the Grignard reaction.

Experimental

A. SYNTHESIS INVOLVING ETHYLENE OXIDE

2-Oxo-3-carboxytetrahydrofuran-3-acetic Acid (I)

Sodium (10 gm.) was dissolved in absolute alcohol (175 cc.) and ethyl malonate (72 gm.) was added. The mixture was cooled and ethylene oxide (20 gm.) slowly added; on prolonged agitation it dissolved. At this stage the separation of a white sodio-derivative occurred with the evolution of a great deal of heat. Good cooling was essential, as, if the temperature rose above 40° C., considerable decomposition occurred. The condensate was allowed to stand overnight and the next day ethyl chloroacetate (55 gm.) was added and the suspension well shaken. After approximately ten minutes the mixture became warm and more mobile, as the sodium chloride separated. The mixture was allowed to react for two days at room temperature, the alcohol removed under reduced pressure, and benzene (200 cc.) added. The benzene solution of the ester was washed twice with water to remove sodium chloride and the benzene removed by distillation. The temperature was raised to 170° (30 mm.) to remove any unused chloroacetic and malonic esters. To the residual ester (83 gm.) 5 N sodium hydroxide solution (190 cc.) and a little alcohol were added and the mixture was refluxed gently for 15 min. The alcohol was removed and the alkaline solution evaporated under reduced pressure and neutralized with 10 N sulphuric acid. The sodium sulphate that separated was removed by filtration and the lactone extracted by means of ether. The ethereal solution was dried over anhydrous sodium sulphate. On evaporation of the ether, crystals of the dibasic acid were left; with a little chloroform these were washed free of oil. The crude acid (18 gm.) was recrystallized twice from glacial acetic acid and washed with chloroform. The pure acid melted at 165°* with decomposition. It was soluble in acetone, acetic acid, alcohol, ether, and water, but insoluble in chloroform and hexane. Found: C, 45.05; H, 4.21%; equivalent weight, 92.9. Calc. for $C_7H_8O_6$: C, 44.68; H, 4.26%; equivalent weight, 94.

The diester of this acid has been isolated in pure condition by distillation *in vacuo*, prior to the saponification. After repeated fractionation, the ester boiled at 204 to 206° (15 mm.). Found: C, 54.00; H, 6.48%; mol. wt., 256. Calc. for $C_{11}H_{16}O_6$: C, 54.10; H, 6.48%; mol. wt., 244.

2-Oxotetrahydrofuran-3-acetic Acid (II)

The dibasic acid (I) isolated as described was heated at 160° C. for about an hour, whereupon the evolution of carbon dioxide ceased. On standing in the ice-box the crude product crystallized. It was purified by boiling with Norite in glacial acetic acid. After a second crystallization from the same solvent it seemed quite pure, melting at 56 to 58°. It was soluble in water, chloroform, acetic acid, ether, and alcohol, but insoluble in hexane and carbon tetrachloride. Found: C, 49.69; H, 5.62%; equivalent weight, 147. Calc. for $C_6H_6O_4$: C, 50.00; H, 5.56%; equivalent weight, 144. Unless crystalline

* Melting points and boiling points are uncorrected.

dibasic acid was employed in this preparation, it was impossible to obtain the lactonic acid as a solid. Preliminary attempts to obtain it by decarboxylation following saponification of the ester, without isolation and purification of the dibasic acid, gave the lactonic acid in the form of an oil boiling at 180 to 195° (11 mm.), which could not be induced to crystallize.

α -(β -Hydroxyethyl)succinamide (III)

Crude 2-oxotetrahydrofuran-3-acetic acid (4 gm.) was dissolved in 95% ethyl alcohol (10 cc.) in a pressure bottle and saturated with ammonia gas at 40° C. The bottle was then stoppered and heated in a water-bath at 100° for four hours. The alcohol and excess ammonia were removed under reduced pressure. On stirring, the residual oil showed signs of solidifying. After two days in the ice-box the solid was freed from oil by washing with a little cold alcohol. The crude diamide (2 gm.) thus obtained was crystallized twice by dissolving it in alcohol and adding acetone. It melted at 137 to 139° with decomposition. The diamide was soluble in water and hot alcohol, but insoluble in acetone, benzene, chloroform, ethyl acetate, and hexane. Found: N, 17.14%. Calc. for $C_6H_{12}O_3N_2$: N, 17.50%.

2-Oxotetrahydrofuran-3-propionic Acid (IV)

Sodium (10 gm.), absolute ethyl alcohol (175 cc.), malonic ester (72 gm.), and ethylene oxide (20 gm.) were treated in a manner similar to that adopted in the previous condensation, ethyl β -bromopropionate (82 gm.) being employed in place of ethyl chloroacetate. The benzene was removed and the residue distilled *in vacuo*. By this means, crude 2-oxo-3-carbethoxytetrahydrofuran-3-propionic ester (61 gm.) boiling at 185 to 235° (11 mm.) was isolated. Repeated fractionation gave a pure sample of this diester boiling at 204 to 206° (15 mm.). Found: C, 55.41; H, 7.18%; mol. wt., 265. Calc. for $C_{12}H_{18}O_6$: C, 55.82; H, 6.95%; mol. wt., 258.

This diester lactone was saponified with 5 N sodium hydroxide solution as before. The alcohol was removed and the alkaline solution was evaporated *in vacuo* to a small volume. The solution was carefully acidified by the introduction of dry hydrogen chloride gas until it was acid to Congo red. The sodium chloride that formed was removed by filtration and the filtrate cooled. On standing, a mass of white needle-like crystals formed. These were dissolved in ether to eliminate inorganic salt. This method of evaporating to a small volume and acidifying was necessary, as the acid was fairly soluble in water and the distribution from water to ether was small. On removal of the ether a pure white residue (30 gm.) was obtained. A small sample of this 2-oxo-3-carboxytetrahydrofuran-3-propionic acid was purified for analysis by dissolving it in ethyl acetate, and adding petroleum ether, whereupon it separated in glistening white needles melting at 125° C. with evolution of carbon dioxide. Found: C, 47.15; H, 4.87%. Calc. for $C_6H_{10}O_6$: C, 47.52; H, 4.95%.

The dibasic acid (25 gm.) just described was decarboxylated on an oil-bath at 160° C. The residue was distilled *in vacuo*, two fractions being

collected: I. B.p. 170 to 200° (12 mm.), 6.2 gm.; II. B.p. 217 to 219° (12 mm.), 10.1 gm. Fraction II, which was very viscous, on standing crystallized in white needles, which were washed with petroleum ether. 2-Oxotetrahydrofuran-3-propionic acid melted at 51.5 to 53°. Found: C, 53.00; H, 6.44%. Calc. for $C_7H_{10}O_4$: C, 53.16; H, 6.33%.

2-Oxo-3-carbethoxy-3-benzyltetrahydrofuran

Benzyl chloride (94.8 gm.) in absolute alcohol (100 cc.) was added to an alcoholic suspension of the sodio-derivative prepared from sodium (17 gm.), malonic ester (120 gm.), and ethylene oxide (33 gm.). Benzene was not used in this preparation. After standing for two days at room temperature the alcohol was removed. On addition of water the sodium chloride dissolved and the ester separated as an oil, which was extracted with ether. After drying over calcium chloride and removal of the ether, the residue was distilled *in vacuo*, the fraction boiling at 185 to 220° (0.5 mm.) being collected. Redistillation gave a product (120 gm.) boiling at 195 to 197° (0.5 mm.). Found: C, 67.55; H, 6.49%; mol. wt., 227. Calc. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.45%; mol. wt., 248.

2-Oxo-3-benzyltetrahydrofuran (γ -Hydroxy- α -benzylbutyrolactone) (V)

The ester (105 gm.) just described was dissolved in alcohol and sodium hydroxide solution (150 cc., 20%) was added. The mixture became quite warm. It was allowed to stand for several days and was then strongly acidified with hydrochloric acid. The oil that separated was extracted with ether, dried, decarboxylated, and distilled *in vacuo*. The fraction (45 gm.) distilling at 140 to 180° (11 mm.) gave on redistillation a pure product boiling at 165 to 166° (10 mm.). Found: C, 74.86; H, 6.88%. Calc. for $C_{11}H_{11}O_2$: C, 75.00; H, 6.82%.

B. SYNTHESSES INVOLVING PROPYLENE OXIDE

2-Oxo-5-methyltetrahydrofuran (γ -Valerolactone) (IX)

Sodium (20 gm.), absolute alcohol (350 cc.), malonic ester (144 gm.), and propylene oxide (54 gm.) were condensed in the manner previously described. The mixture was refluxed with 5*N* sodium hydroxide solution for an hour to hydrolyse the ester (VI). The alcohol was removed and the solution evaporated *in vacuo* to a small volume. The solution was carefully acidified with hydrochloric acid and extracted with ether. Presumably this ethereal solution should contain the acid lactone (VIII). However, the lactone could not be isolated, as during both the acidification and the attempts to distil the solution carbon dioxide was lost. Attempts to produce a diamide from this lactone in the usual manner resulted in decarboxylation, with the production of ammonium carbonate. A similar result has been noted previously by McRae, Charlesworth, and Alexander (9) with 2-ketocyclohexylmalonic acid. However, if prior to acidification a concentrated solution of barium chloride was added to the solution of the sodium salt an insoluble

barium salt of the dibasic acid (VII) was precipitated. Found: Ba, 46.41%. Calc. for $C_6H_8O_5Ba$: Ba, 46.20%.

The impure lactone (VIII) was decarboxylated at 160° C. on an oil-bath. The residue was dissolved in ether and washed with sodium carbonate solution, and the ethereal extract was dried over anhydrous sodium sulphate. On distillation three fractions were collected: I. B.p. up to 85° (13 mm.), 2.5 gm.; II. Boiling at 85 to 95° (12 mm.), 14.5 gm.; III. Boiling at 95 to 103° (13 mm.), 4.5 gm. Redistillation of Fraction II produced a colourless oil (13.5 gm.) boiling at 83 to 84° (12 mm.). This is in agreement with the boiling point of 83 to 84° (13 mm.) given for γ -valerolactone by Leuchs and Möbis (7) and by other workers (1, 8, 11, 12). Found: C, 60.1; H, 7.7%. Calc. for $C_6H_8O_2$: C, 60.0; H, 8.0%.

The amide of this γ -valerolactone was prepared by the method of Boorman and Linstead (1) by treatment of the acid with aqueous ammonia (*d.*, 0.88). It crystallized from chloroform in white needles melting at 51.5° C. Boorman and Linstead (1) record a melting point of 51.5 to 52°, and Neugebauer (10), 50° for this amide.

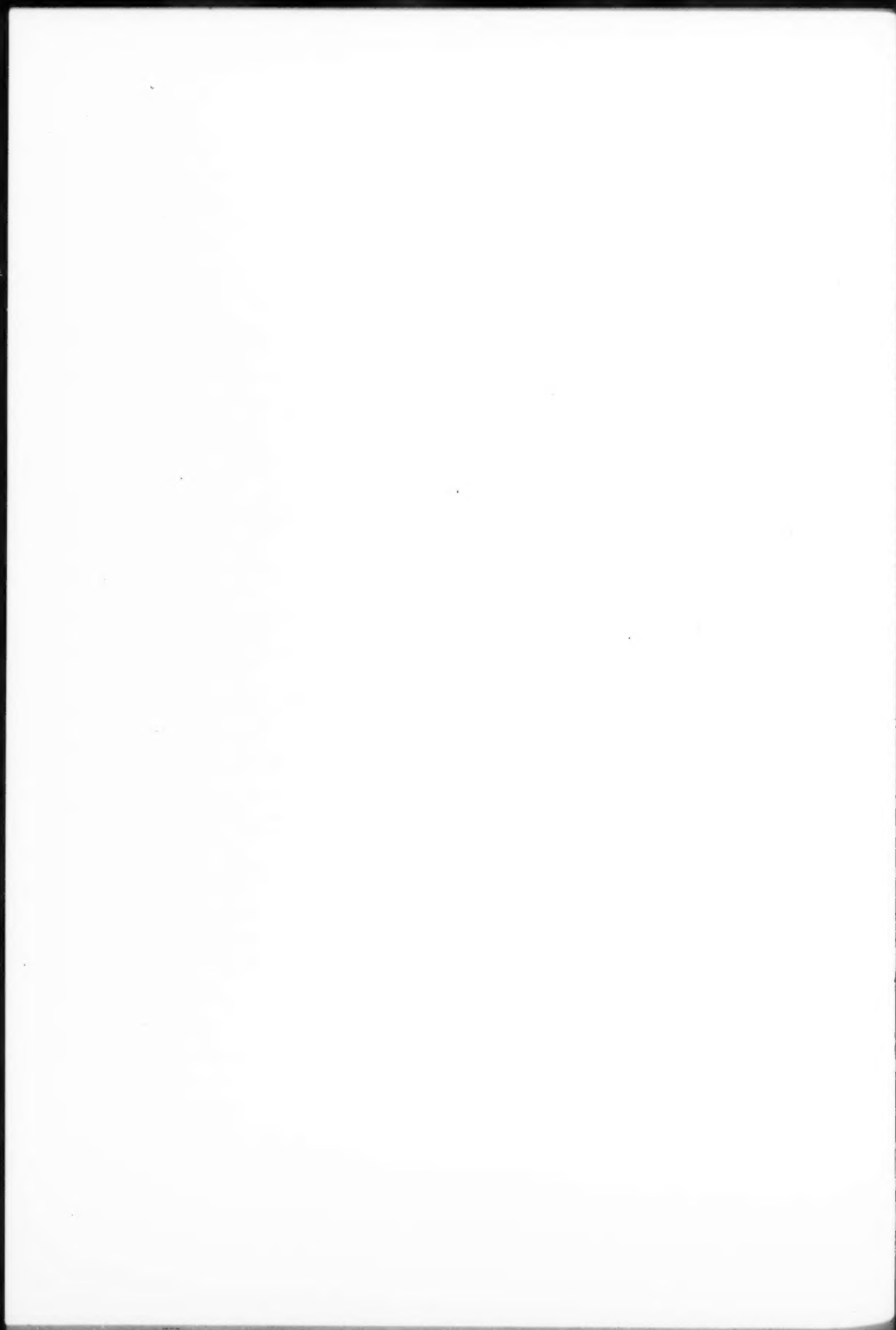
If the sodium derivative (VI) from the original condensation was not hydrolysed with sodium hydroxide, but acidified directly with 10 *N* sulphuric acid and extracted with ether, the lactone of γ -hydroxy- α -carbethoxy-valeric acid was produced. An attempt to distil this ester was not very successful, as the ester decomposed partially during the boiling, causing a fluctuation of pressure. The boiling point was recorded as 125 to 135° (25–40 mm.). Found: C, 54.24; H, 7.45%. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 6.98%. On hydrolysis of this ester, acidification, and decarboxylation γ -valerolactone was isolated as before.

2-Oxo-5-methyltetrahydrofuran-3-propionic Acid (XI)

Sodium (17.2 gm.), ethyl malonate (120 gm.), propylene oxide (43.5 gm.), and ethyl β -bromopropionate (135 gm.) were condensed in the usual manner in absolute alcohol. The alcohol was removed, water added, and the resulting oil taken up in ether. After drying and removal of the ether, the residue was distilled *in vacuo*, the fraction boiling at 195 to 215° C. (9 mm.), 14.8 gm., being collected. This ester (X) was dissolved in alcohol and allowed to stand for a day at room temperature with 20% sodium hydroxide solution (230 cc.). After acidification and concentration it was extracted with ether. After evaporation of the ether, the residue readily lost carbon dioxide on warming. After decarboxylation it was distilled *in vacuo* and an amber coloured oil (75 gm.), b.p. 175 to 240° (10 mm.), collected. On standing, white crystals formed; these were separated from the remaining oil and washed carefully with a little ether. The specimen of 2-oxo-5-methyltetrahydrofuran-3-propionic acid melted at 54 to 56°. Found: C, 55.00; H, 7.12%. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 6.98%.

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